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(54) LEAD-FREE SOLDER ALLOY AND ELECTRONIC CIRCUIT DEVICE USING IT

(57)Abstract:
PROBLEM TO BE SOLVED: To miniaturize and disperse intermetallic compound and obtain a lead-free solder alloy holding the reliability of fine solder connected part and having low m.p., good wettability and non-environmental pollution by specifying the composition of the lead-free solder alloy.
SOLUTION: This lead-free solder alloy is composed of by weight, >6% to 11% Zn, 4-12% In, 0.5-3% Ag and the balance Sn with inevitable impurities. Since this lead-free solder material does not contain harmful lead, this solder is safely used. Further, since this solder has the same degree of m.p. as that of an ordinary used Sn-Pb eutectic solder alloy, this solder can be applied to the ordinary electronic parts and a printed wiring substrate in view of the heat resistance.

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%
[0009] flux

1-4,
7-9

FULL CONTENTS

[Claim(s)]
[Claim 1] The unleaded solder characterized by exceeding 6% and 3% or less of silver (Ag) and the remainder serving as 11% or less of zinc (Zn), and 4% or more of indium [12% or less of] (In) from tin (Sn) and the impurity mixed unescapable 0.5% or more by weight %.
[Claim 2] The unleaded solder characterized by exceeding 6% and the remainder serving as 11% or less of zinc (Zn), and 4% or more of indium [12% or less of] (In) and 0.5% or more of antimony [3% or less of] (Sb) from tin (Sn) and the impurity mixed unescapable by weight %.
[Claim 3] By weight %, exceed 6% and 11% or less of zinc (Zn), and 4% or more 12% or less of indium (In), The unleaded solder characterized by the remainder serving as 3% or less of silver (Ag), and 0.5% or more of antimony [3% or less of] (Sb) from tin (Sn) and the impurity mixed unescapable 0.5% or more.
[Claim 4] Electronic circuit equipment which connects electronic parts to any 1 term of Claim 1 or Claim 3 using the solder of a description, and is characterized by things.
[Claim 5] It is electronic circuit equipment characterized by bonding of electronic parts being bonding of the semiconductor device to a printed-circuit board or ceramic layered substrate top, bonding of an I/O pin, or hermetic sealing in Claim 4.

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the unleaded solder which does not contain lead, and

especially Bonding of electronic parts, For example, it is related with the electronic circuit equipment produced using the pollution-free unleaded solder and pollution-free it which are used suitably for bonding of semiconductor devices, such as LSI to a printed-circuit board and ceramic layered substrate top, bonding of an I/O pin, or hermetic sealing.

[0002]

[Description of the Prior Art] The solder which consists of tin (Sn) and lead (Pb), and especially the solder whose Pb consists of 7 weight % 63weight % in Sn are widely used for bonding of electronic parts. Since this has the amount of [that the fusing points of this solder are 183 degrees C and low temperature, and] comparatively flexible terminal area, it can absorb the heat strain generated in a terminal area for every ON and OFF of an electrical and electric equipment, and depends it on the Reasons nil why the reliability of a terminal area is securable etc. However, when the electrical and electric equipment using this solder is discarded in the earth, Pb harmful to a human body is eluted depending on an environmental condition, and ground water is polluted. Therefore, to be the alloy which does not contain a metal harmful to human bodies, such as Pb, is demanded. Moreover, the heat-resisting property of electronic parts or a printed-circuit board to this alloy needs to have a fusing point comparable as the conventional Sn-Pb solder. U.S. Pat. No. 5242658 is mentioned to what was developed as a solder which is an alloy which does not contain Pb and has a fusing point comparable as the conventional Sn-Pb solder from such a viewpoint. Moreover, a fusing point is the alloy which does not contain Pb from conventional Sn-Pb solder although it is an elevated temperature, and JP,H6-238479,A is mentioned as a solder which raised especially the mechanical property.

[0003]

[Problem to be solved by the invention] [the U.S. Pat. No. 5242658 number which is the conventional technique] By weight (wt) %, Sn consists of a presentation which contains less than more than (Zinc Zn) 6.7%19.2% and less than more than indium (In)2.7%16.4% 89.4% or less 72.8% or more, and mentions Sn83.6%, Zn7.6%, and In8.8% as a desirable presentation especially. The fusing point of the alloy of this desirable presentation is 181-187 degrees C (the liquidus temperature to which 181 degrees C and the dissolution end the solidus temperature which an alloy begins to dissolve is 187 degrees C), and since it is comparable as the fusing point of the conventional Sn-Pb system solder, the problem is carried out if not generated. However, the above-mentioned alloy has the problem shown below in the reliability of the soldered joint of electronic parts. That is, the solidification structure by the metallographic microscope photograph of an Sn83.6%, Zn7.6%, and In8.8% alloy is shown in drawing 9 . The large-sized needle crystal 11 which amounts to several millimeters in length is growing so that clearly from drawing. When this kind of solder is applied to the detailed soldered joint of electronic parts By ON and OFF of the electrical and electric equipment, the thermal stress or heat distortion generated in a soldered-joint part concentrated on the needle crystal part of the above-mentioned large form, and since there was a possibility that stress destruction might be carried out at an early stage, there was a problem that it was difficult to secure the reliability of a soldered-joint part. Moreover, although JP,H6-238479,A is the solder of an Sn(remainder)-Ag(1 - 6wt%)-Zn (0.2 -

6.0wt%) system which aimed at the betterment of a mechanical property, especially creep resistance characteristics, a fusing point is an elevated temperature from conventional Sn-Pb solder.
[0004] The object of this invention cancels the trouble in the above-mentioned conventional technique, and does not have growth of a large-sized needle crystal. Wettability is good at the low-melt point point that miniaturize an intermetallic compound, it is made to distribute and the reliability of a detailed soldered-joint part can be secured, and it is in offering the electronic circuit equipment connected using the unleaded solder of a pollution-free and new presentation, and it.
[0005]
[Means for solving problem] In order to attain the object of above-mentioned this invention, this invention is considered as architecture like a description at Claims. Like the description to Claim 1, this invention is weight %, exceeds 6%, and Namely, 11% or less of zinc (Zn), The remainder carries out to 4% or more of indium [12% or less of] (In), and 0.5% or more of silver [3% or less of] (Ag) with the unleaded solder which consists of tin (Sn) and an impurity mixed unescapable. Like the description to Claim 2, this invention is weight %, exceeds 6%, and Moreover, 11% or less of zinc (Zn), The remainder carries out to 4% or more of indium [12% or less of] (In), and 0.5% or more of antimony [3% or less of] (Sb) with the unleaded solder which consists of tin (Sn) and an impurity mixed unescapable. Like the description to Claim 3, this invention is weight %, exceeds 6%, and Moreover, 11% or less of zinc (Zn), The remainder carries out to 4% or more of indium [12% or less of] (In), and 0.5% or more of silver [3% or less of] (Ag) and 0.5% or more of antimony [3% or less of] (Sb) with the unleaded solder which consists of tin (Sn) and an impurity mixed unescapable. Moreover, this invention is a thing according to claim 4 which connects electronic parts to any 1 term of Claim 1 or Claim 3 using the solder of a description, and is used as electronic circuit equipment like. Moreover, this invention is a thing according to claim 5 which makes bonding of electronic parts bonding of the semiconductor device to a printed-circuit board or ceramic layered substrate top, bonding of an I/O pin, or the electronic circuit equipment that carried out hermetic sealing in Claim 4 like. The unleaded solder of this invention is weight % like the description to above-mentioned Claim 1 or Claim 3 at the alloy of a Sn-Zn system. By adding 3% or less for Ag 0.5% or more, and adding 3% or less, or Ag and Sb for Sb 3% or less 0.5% or more 0.5% or more, respectively, inhibition of growth of a needle crystal or the miniaturization of an intermetallic compound is attained, and there is an effect which can improve the hardness of a soldered-joint part further.
[0006] Setting out of the component composition of the unleaded solder which does not contain Pb of this invention is based on the following views. First, the metal used as a base material was set to Sn in consideration of the wettability of solder to the meta-rise of electronic parts. However, the problem of 232 degrees C and working temperature being as high as near 260 degree C, and exceeding the heat-resistant limitation (near 230 degree C) of a print plate produces the fusing point of Sn. Therefore, in order to form Sn and an eutectic and to reduce a fusing point, it considered adding Zn. Zn -- 9wt% -- if it adds, a fusing point will serve as a Sn-Zn eutectic alloy which is 199 degrees C. However, this Sn-Zn eutectic alloy still had the slightly high fusing point, and indium (In) was added in

order to solve this fusing point and a wettable problem, since the wettability to the meta-rise of electronic parts is [the effect of the oxide film of Zn] bad. In has the effect of reducing the fusing point of this alloy further, and the effect of raising the wettability to the meta-rise of electronic parts. However, an above-mentioned Sn-Zn-In alloy forms a large-sized needle crystal, and there is a problem on which the reliability of the soldered joint of electronic parts is reduced. In order to improve this point and to raise the hardness of a soldered joint, the range of the description of Claim 1 or Claim 3 is made to carry out addition inclusion of Ag, Sb, or its both. In consideration of the effect of reducing a fusing point with an eutectic with Sn, Zn was weight %, exceeded 6% and could be 11% or less. Moreover, although In improves the wettability to the meta-rise of electronic parts and a fusing point is reduced Since the low fusing point phase (about 105 degrees C of fusing points) of a Sn-Zn-In alloy will appear if it adds so much, in order to avoid this and to make a fusing point into near 185 degree C of the original object, the addition was made into 12% or less 4% or more. Ag could be 3% or less 0.5% or more in order to form a large-sized needle crystal with Sn while a fusing point will go up, if an addition increases. Since a solder became hard while a fusing point will go up, if an addition increases, Sb could be 3% or less 0.5% or more. The unleaded solder of this invention is weight % as a more desirable presentation from viewpoints, such as inhibition of the wettability to a fusing point and a meta-rise, and a needle crystal, and a miniaturization of an intermetallic compound. The solder which contains 1.5 to 2.5%, respectively is mentioned in 80 to 82% of Sn, 6.5 to 8.5% of Zn, 9 to 11% of In, 1.5 to 2.5% of Ag, 1.5 to 2.5% of Sb, or Ag and Sb. Furthermore, the solder which includes the neighborhood 2%, respectively is mentioned as the most desirable presentation near Sn81%, near Zn7%, near In10%, near Ag2%, near Sb2%, or in Ag and Sb. In addition, as an operation of each element added to the above-mentioned Sn-Zn alloy, In improves the wettability to the meta-rise of electronic parts while reducing a fusing point. Moreover, since Ag miniaturizes a large-sized needle crystal and forms a small Sn-Ag intermetallic compound, it is effective in this being distributed by the soldered-joint part and connection resilience improving. Moreover, since Sb miniaturizes a large-sized needle crystal, it is effective in raising the connection resilience of solder.

[0007]

[Mode for carrying out the invention]

<Form of the first operation> Sn, Zn, In and Sb of 99.9% of purity, and Ag are prepared first. Respectively it mixes so that Sn81%, Zn7%, In10%, and Ag2% may become comparatively, and in the atmosphere of nitrogen, it mixes and fuses uniformly, it cools by weight %, and let this be an ingot. Next, it is verified whether they are whether it has the characteristic which this alloy made the original target, and no. First, a part of [a little] above-mentioned ingot is shaved off, and the fusing point of an alloy is measured with differential-calorimetry equipment. The result is shown in drawing 2 R> 2. Solidus temperature is 173 degrees C, liquidus temperature is 200 degrees C, and it turned out that it has the around 185-degree C proper fusing point made into the original target. Next, in order to clarify the organization of this alloy, mirror polishing of a part of above-mentioned ingot is carried out, and the result observed with the metallographic microscope is shown in drawing 1 . At drawing 9

shown as a conventional example, the intermetallic compound 12 is miniaturized and distributed with the alloy by the form of this operation to the large-sized needle crystal existing. In the detailed soldered joint of electronic parts, when heat distortion and thermal stress occur in a soldered-joint part for every ON and OFF of the power of electronic circuit equipment, along with the large-sized needle crystal 11 shown in the conventional example, it is easy to be destroyed, and the reliability of the electronic item which carried out the soldered joint is not guaranteed. On the other hand, in the unleaded solder of this invention, since the small intermetallic compound is distributing, the stress destruction by the conventional large-sized needle crystal is not generated.

[0008] <Form of the 2nd operation> Next, the solder of the presentation containing Sn81%, Zn7%, In10%, and Sb2% was produced like the form of the 1st operation by weight %. This solder verifies whether they are whether it has the characteristic made into the original target, and no. First, a part of [a little] above-mentioned ingot was shaved off, and the fusing point of the alloy was measured with differential-calorimetry equipment. The result is shown in drawing 4 . In drawing, solidus temperature is 162 degrees C, liquidus temperature is 192 degrees C, and it turned out that it has a proper fusing point. Furthermore, in order to clarify the organization of the above-mentioned alloy, mirror polishing of a part of above-mentioned ingot is carried out, and the result observed with the metallographic microscope is shown in drawing 3 . As shown in drawing, it turned out that a small intermetallic compound distributes and exists and the solder excellent in the bonding reliability of electronic parts is obtained.

[0009] <Form of the 3rd operation> The ingot which consists of Sn80%, Zn7%, In10%, Ag1%, and Sb2% of presentation was produced like the form of the 1st operation by weight %. First, a part of [a little] above-mentioned ingot was shaved off, and the fusing point of the alloy was measured with differential-calorimetry equipment. The result is shown in drawing 6 . Solidus temperature is 175 degrees C, liquidus temperature is 199 degrees C, and it turned out that it has a proper fusing point. Furthermore, in order to clarify the organization of this alloy, mirror polishing of a part of this ingot is carried out, and the result observed with the metallographic microscope is shown in drawing 5 R> 5. As shown in drawing, it turned out that a small intermetallic compound distributes and exists and it excels in the reliability of a soldered joint. Next, the above-mentioned ingot was powdered, it mixed with flux to homogeneity, and the cream-like soldering paste was produced. This was applied on the copper pattern for soldering of a printed-circuit board using the screen etc., and the soldered joint was carried out by arranging the electronic parts corresponding to a this top, and carrying out heat melting at 220 degrees C among nitrogen-gas-atmosphere mind. A general view of the electronic-parts equipment after bonding is shown in drawing 7 .

[0010] <Form of the 4th operation> The ingot which consists of Sn81%, Zn7%, In10%, and Ag2% of presentation was produced like the form of the 1st operation by weight %. Based on this, the solder ball about 0.2 millimeter in diameter was produced. The method of producing a solder ball was produced by making mist form blow off from the head of a nozzle, and carrying out cooling coagulation of the melting solder in oil. Next, the solder bump was formed by carrying out alignment

loading with flux and heating a solder ball in nitrogen-gas-atmosphere mind to the electrode end child for soldered joints of LSI, at about 220 degrees C. Next, this LSI with a solder bump was carried out on the electrode end child for soldering of a printed-circuit board, the solder bump was turned down, it has arranged with flux, and the soldered joint was heated and carried out to about 220 degrees C in nitrogen-gas-atmosphere mind. The appearance of the electronic-parts equipment after bonding is shown in drawing 8 . Although LSI was carried on the printed-circuit board and it connected with the form of this operation, you may make loading bonding on a ceramic layered substrate instead of a printed-circuit board. Moreover, the components to carry are not limited to LSI.

[0011]

[Effect of the Invention] Since the unleaded solder ingredient of this invention does not contain harmful lead, it is used for insurance. Moreover, since it has a fusing point comparable as the Sn-Pb eutectic solder currently used from the former, it is applicable from a heat-resistant viewpoint also to conventional electronic parts and a conventional printed-circuit board. Furthermore, there is no formation of a large-sized needle crystal, and since an intermetallic compound can be miniaturized and it can be made to distribute, the reliability of the detailed soldered-joint part of electronic parts is securable.

[Brief Description of the Drawings]

[Drawing 1] The sketch drawing figure of the metallographic microscope photograph in which the organization of an unleaded solder which illustrated with the form of operation of the 1st of this invention is shown.

[Drawing 2] Drawing showing the fusing point by the differential-calorimetry result of the unleaded solder illustrated with the form of operation of the 1st of this invention.

[Drawing 3] The sketch drawing figure of the metallographic microscope photograph in which the organization of an unleaded solder which illustrated with the form of operation of the 2nd of this invention is shown.

[Drawing 4] Drawing showing the fusing point by the differential-calorimetry result of the unleaded solder illustrated with the form of operation of the 2nd of this invention.

[Drawing 5] The sketch drawing figure of the metallographic microscope photograph in which the organization of an unleaded solder which illustrated with the form of operation of the 3rd of this invention is shown.

[Drawing 6] Drawing showing the fusing point by the differential-calorimetry result of the unleaded solder illustrated with the form of operation of the 3rd of this invention.

[Drawing 7] The perspective view showing the appearance of the electronic circuit equipment connected using the unleaded solder illustrated with the form of operation of the 3rd of this invention.

[Drawing 8] The perspective view showing the appearance of the electronic circuit equipment

connected using the unleaded solder illustrated with the form of operation of the 4th of this invention. The general-view figure of the electronic circuit equipment connected using the solder of one example of this invention.

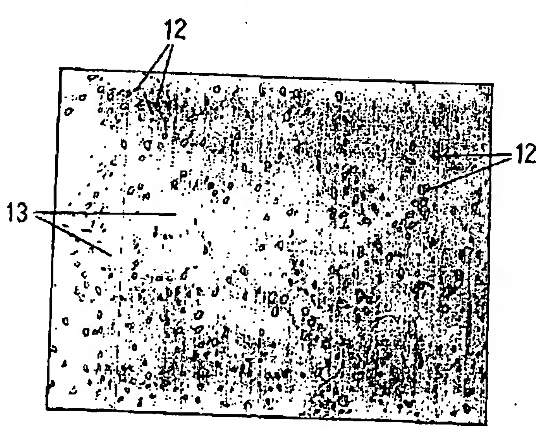
[Drawing 9] The sketch drawing figure of the metallographic microscope photograph in which an example of the organization of the conventional unleaded solder is shown.

[Explanations of letters or numerals]

1 -- Printed-circuit board
2 -- Electronic parts
3 -- Soldered-joint part
4 -- Electronic parts
5 -- Soldered-joint part
6 -- Electronic parts
7 -- Soldered-joint part
8 -- Printed-circuit board
9 -- LSI
10 -- Terminal area by a solder ball
11 -- Needle crystal
12 -- Intermetallic compound
13 -- Solid solution

[Drawing 1]

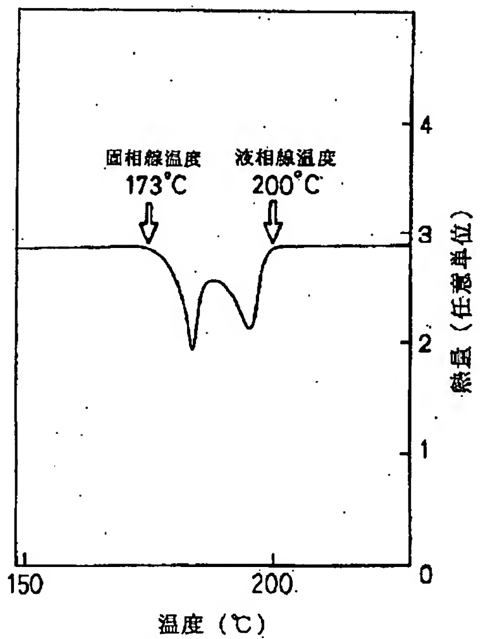
図 1



12…金属間化合物
13…固溶体
0.1mm

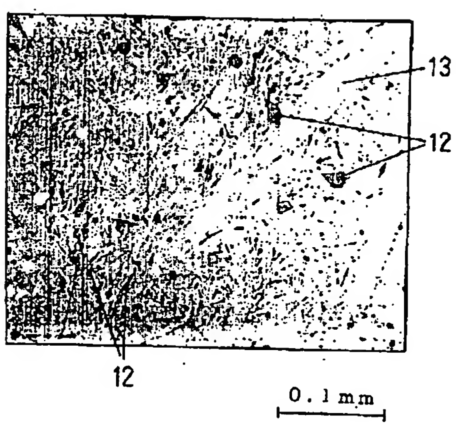
[Drawing 2]

図 2



[Drawing 3]

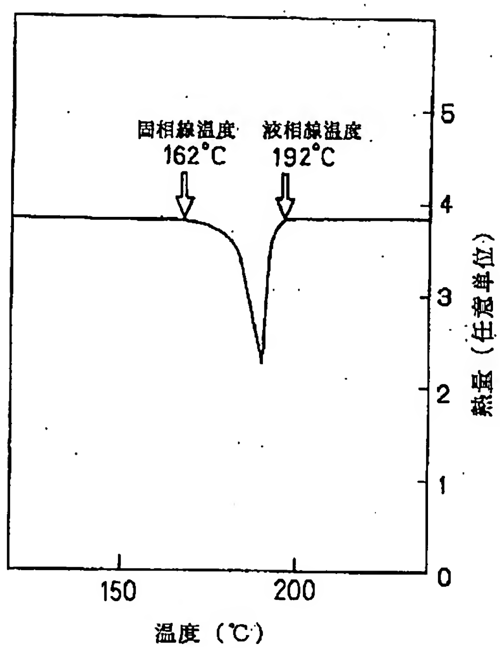
図 3



1 2 …金属間化合物
1 3 …固溶体

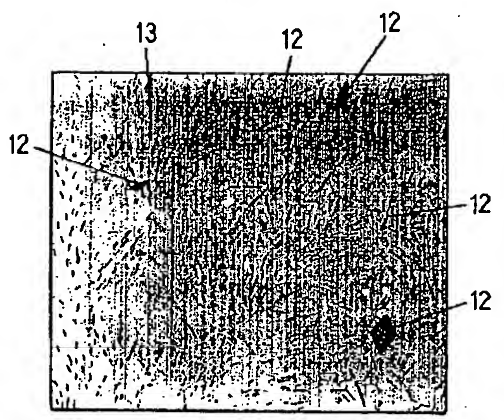
[Drawing 4]

図4



[Drawing 5]

図5



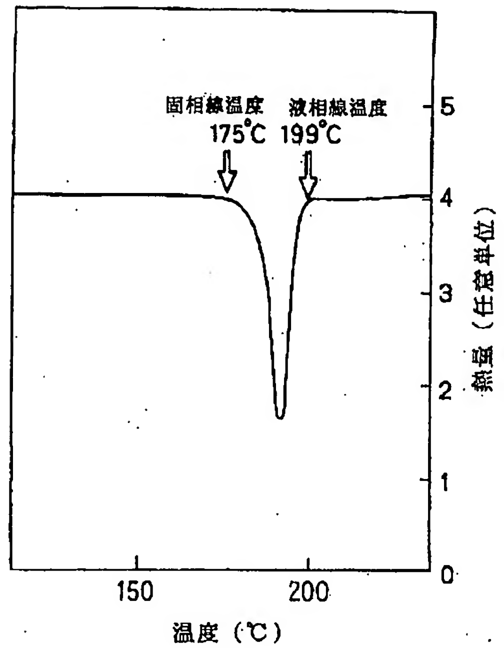
1 2 …金属間化合物

1 3 …固溶体

0.1mm

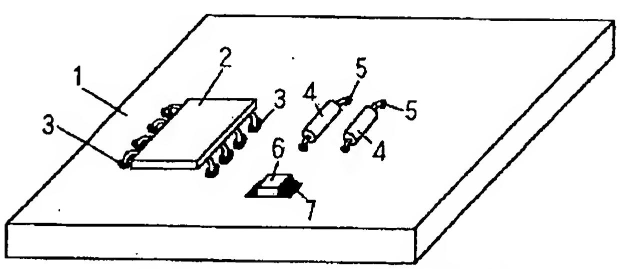
[Drawing 6]

図 6



[Drawing 7]

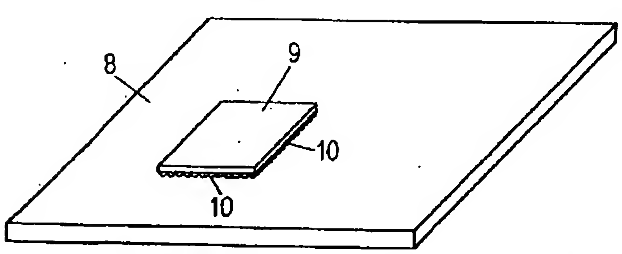
図 7



1…プリント配線基板
2…電子部品
3…はんだ接続部
4…電子部品
5…はんだ接続部
6…電子部品
7…はんだ接続部

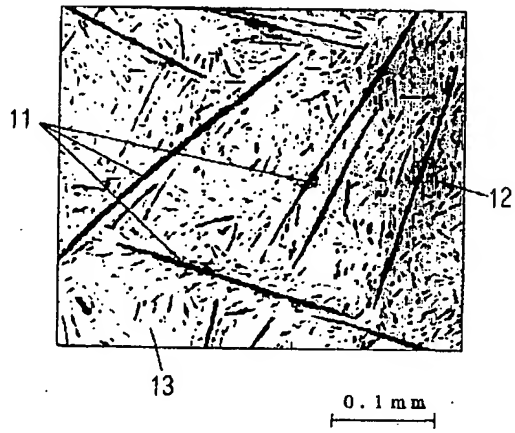
[Drawing 8]

図 8



8…プリント配線基板
9…ＬＳＩ
１０…はんだボールによる接続部

図 9



1 1…針状結晶
1 2…金属間化合物
1 3…固溶体

[Drawing 9]

[Translation done.]